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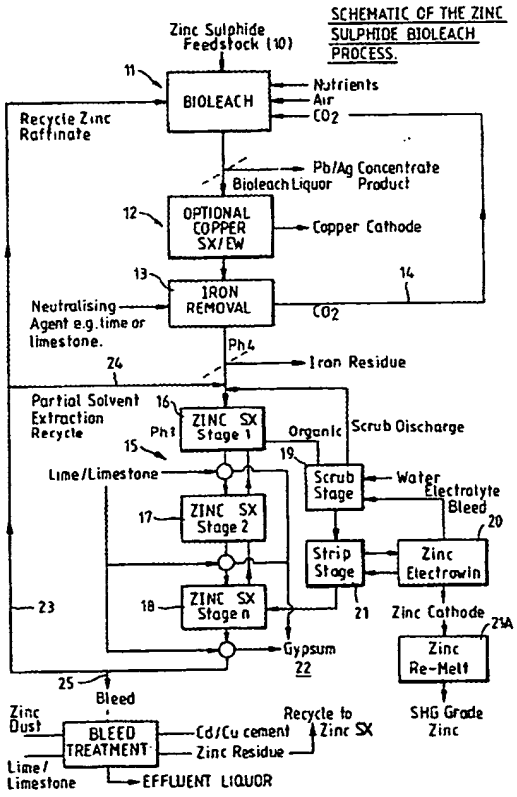
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(54) Title: AN INTEGRATED BIOLEACH/SOLVENT EXTRACTION PROCESS FOR ZINC METAL PRODUCTION FROM ZINC CONCENTRATES

(57) Abstract

Zinc is recovered by an integrated bioleaching, solvent extraction system where the aqueous raffinate from the solvent extraction stage is recycled to the bioleach stage. Operating costs are significantly reduced, pressure vessels are not required, energy costs are reduced, low cost reagents can be used, no gaseous effluents are produced and all by-products can be sold or efficiently stored.



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TITLE

An Integrated bioleach/solvent extraction process for zinc metal production from zinc concentrates.

FIELD OF THE INVENTION

THIS INVENTION relates to a method and apparatus for separating zinc from zinc concentrates, and is particularly directed to a method to separate zinc from low grade zinc sulphide concentrates.

BACKGROUND ART

Zinc is a metal which generally exists in an oxidised form, and therefore complexed with various other groups. Commonly, zinc exists as zinc sulphide, oxide and carbonate. Therefore, to produce zinc metal, it is necessary to treat the zinc compounds in the most cost effective manner.

It is known to refine zinc by smelting zinc sulphide concentrates. This technique is mainly applicable to mixed lead/zinc concentrates but can treat some zinc concentrates directly. The smelting technique involves sintering of the lead/zinc concentrate with the addition of coke, followed by smelting of the sinter in a bath of molten lead. The final zinc product contains up to 1% lead, and can be further upgraded to SHG grade zinc via distillation in a retort. One of the disadvantages with this technique, is the large energy cost involved in the smelting process. There are also high operating costs caused by the high cost of unit input (such as coke), and high manpower maintenance and energy costs. The high capital costs in constructing new refineries is also a disadvantage.

A second known technique is a hydrometallurgical system. Hydrometallurgical systems have mainly been developed for treating high grade zinc sulphide concentrate feeds, and today constitute over 80% of commercial zinc production. The major systems developed are the traditional Roast/Leach refinery and more recently Pressure Leach systems, such as that developed by Sherritt Gordon in Canada. A range of Roast/Leach

commercial operations exist, their classification mainly occurring on the basis of the technique employed for removing iron from the system. These classifications are briefly the Jarosite Process, the Goethite Process and the Hematite Process. Roast/Leach Plants can only take as feedstock limited tonnages of Lead/Zinc or low grade Zinc concentrates.

Pressure Leaching using oxygen at elevated pressures and temperatures has been developed as a cheaper alternative for treating high grade zinc sulphide concentrates, and can significantly reduce capital and operating costs. Again, however, the technology is not as yet applicable to low grade zinc sulphide feeds containing significant quantities of lead, mainly because of high acidity requirements and sulphur separation difficulties. In addition, impurities can be a problem in subsequent purification and refining stages.

A more recent alternative leaching system for treating mixed Lead/Zinc Sulphide Concentrates are chloride based systems, as typified by the CANMET, MINIMET and USBM processes. These processes, although technically feasible, have not progressed to commercial operations, chiefly because of their complexity and operating difficulties. They are not as yet a viable alternative to the existing Roast/Leach or Pressure Leach technologies.

The major problem with existing technologies is the high capital and operating costs entailed for a commercial operation. High capital costs are mainly due to the complexity of the current processes. High operating costs are caused by both the high cost of unit inputs (such as coke for ISF Plants) and high manpower and maintenance costs. This limits the construction of new refineries, and, particularly at low zinc prices, means that many operating plants are unprofitable.

In addition to economic factors, the following major problems occur with existing technologies:

(1) Roast/Leach and Pressure Leach Plants cannot handle

low grade Zinc Concentrates or mixed Lead/Zinc Concentrates as a primary feedstock.

(2) Current Leach Plants producing zinc metal involve considerable technical difficulty and complexity in purifying zinc electrolyte prior to electrowinning. They have particular problems with high levels of impurities such as magnesium, halogens, germanium, and thallium in the feed. ISF Plants often have limited tolerance to high elemental sulphur levels.

(3) The high degree of complexity and high maintenance requirements of existing processes means that plant availabilities are often low.

(4) Current processes often result in substantial environmental difficulties. Both Roast/Leach and ISF Plants result in SO2 emissions, which generally requires conversion to sulphuric acid. This is expensive, generally uneconomic, and in many parts of the world difficult because of overcapacity of production. In addition, increasingly stringent sulphuric acid standards (such as very low mercury specifications), will mean that substantial additional capital will require installation to meet the standards.

In addition to gaseous effluent problems, severe liquid and solid disposal problems exist. Most solid residues are toxic and require extensive landfills or expensive residue treatment (such as KIVCET or QSL furnace treatment to produce impure zinc oxides). Leaching plants generally require a liquid phase bleed for magnesium or sulphate control, resulting in substantial operating costs or zinc revenue losses.

In summary, the existing technologies are expensive, both in capital and operating costs, and apart from ISF furnaces, not in general applicable to mixed Lead/Zinc or low grade Zinc Concentrates. The current invention has been particularly targeted to an economic treatment option for these feedstocks.

More recently, the use of micro-organisms to leach

zinc from a concentrate and into an aqueous solution has been investigated. It is known that certain micro-organisms (ie. Thiobacillus Ferrooxidans), under acidic conditions, can solubilise zinc by converting zinc sulphide, in the presence of oxygen, to the zinc anion and the sulphate cation. This bioleach technique can be used at room temperature, or slightly above room temperature, and at atmospheric pressure (ie. no pressure vessels required). Under controlled conditions, up to 80 - 120 g/l of zinc can be extracted into solution. The bioleach technique is not selective only to zinc, and will also solubilise copper, cadmium and some iron. Although the level of zinc in solution approximates that which is suitable for electrowinning (electrowinning requiring a zinc level of between 80 - 160 g/l), the impurities in the zinc solution makes a direct electrowinning step unfeasible. To reduce the impurities, an extensive and expensive purification circuit is required. Therefore a direct bioleaching-electrowinning system is not yet practical.

OBJECT OF THE INVENTION

The present invention has been developed to provide a method by which zinc and particularly zinc metal can be separated or obtained from zinc concentrates, and especially from lower grade zinc sulphide concentrates, in a manner which can minimise input costs, and unusable waste products. The method is also energy efficient when compared to the smelting and roast/leach techniques, and also does not produce toxic products such as sulphur dioxide.

In one form, the invention resides in a method for separating zinc from zinc concentrates, the method comprising the steps of subjecting the zinc concentrate to a bioleach step to form a solution containing zinc, at least partially removing the zinc from the solution, and returning at least part of the zinc depleted solution to the bioleach step.

By combining the bioleach step, with the zinc

removal step, and returning the solution to the bioleach step after zinc has been removed therefrom, it is found that the zinc can be removed from the zinc concentrate in a low cost and effective manner.

The zinc concentrate may include low grade lead/zinc or low grade zinc concentrates which to date have been difficult or uneconomic to process. Typically, the zinc concentrate is a zinc sulphide concentrate which can contain lead, copper and iron containing minerals. The zinc sulphide concentrates may include sphalerite, marmatite or concentrates containing:

(1) Zinc oxides and carbonates (such as zincite or smithsonite),

(2) Lead sulphides, oxides or mixed compounds (such as galena, anglesite or plumbate),

(3) Iron containing sulphides, carbonates and oxides (such as pyrite, pyrrhotite, siderite and hematite),

(4) Copper containing sulphides, carbonates and oxides (such as chalcopyrite, chalcocite, covellite, cuprite and malachite),

(5) Cadmium containing sulphides, carbonates and oxides (such as greenockite),

(6) Calcium, magnesium and aluminium containing minerals (such as dolomite, calcite, magnesite and alumina),

(7) Gold and silver containing minerals (such as argentite).

The invention can provide an economic and novel technique for treating the above concentrates to produce as products; zinc metal, copper metal, a lead/silver/gold concentrate, saleable gypsum, and a cadmium/copper cement. Using the present method, a readily disposable, compact iron and aluminium containing residue can be the only waste product, therefore eliminating or substantially reducing toxic waste products.

The feed stock (ie. the zinc concentrate), may be initially ground to a small particle size, to improve its surface area.

The process can take as feedstocks, concentrates

with a zinc content up to 85% by mass, sulphur content to 50%, lead content to 50%, copper content to 5%, cadmium content to 1% and magnesium, calcium and aluminium contents up to 1%. Any quantities of gold and silver can be employed. More specifically, the concentrate should contain metal values in the range 20-60% Zinc, 0-20% Lead, 20-40% Sulphur and 5-20% Iron.

The feedstock may be contacted with one or more micro-organisms in a vessel or tank. The bioleach step may be conducted under aerobic conditions, and suitably with agitation. The bioleach step may also be conducted under acidic conditions, and a preferred range of pH is from about 0.5 to about 2.5. The bioleach step may be conducted over a range of temperatures, and times, and suitably the temperature can range between 20 - 80°C. The residence time depends on the feedstock and solids concentration and can be in the range of 0.3 - 8 days. The feedstock is preferably slurried with recycled solution from the solvent extraction step before or during the bioleach step.

The micro-organisms may be a mixture of the aerobic autotrophs Thiobacillus Ferrooxidans and Leptospirillum Ferrooxidans. Preferably, the mixture is T. Ferrooxidans, L. Ferrooxidans, Thiobacillus Thiooxidans, Sulfobacillus strains and mixed heterotrophic organisms. The preferred bioleach temperature is 35 - 50°C.

The reactor units may consist of one or more agitated, aerated reactors which can be connected in series or parallel. Aeration should be sufficient to provide adequate oxygen for the bacterial oxidation, typically 0.05 to 1 vvm (volume of gas/volume of reactor - minute). In order to enhance the bacterial leaching, a carbon dioxide supplement can be provided with the air. This can be in the range 0-5%, typically about 2%. In order to reduce costs, this carbon dioxide can be supplied from carbon dioxide liberated during an iron precipitation stage, if limestone or magnesium carbonate is used for neutralisation. If desired, part

of the product slurry, solids or solution can be recycled to enhance bioleaching, and improve metal value recoveries.

The bioleach step can be further enhanced by providing additional nutrients with the solid feed, particularly nitrogen, phosphates and potassium. The level of addition depends on the extent of such nutrients in the original feed solids. However, typically up to 0.5 gpl of ammonium and phosphate containing salts has been found to accelerate bioleaching. An additional enhancer for certain feedstocks is the addition of ferrous ions, particularly for feedstocks with low pyrite contents. Up to 5 gpl Fe^{2+} when added to the feed can stabilise the bioleach, and thus can improve overall metal extractions.

It is found during the bioleach process that zinc, copper, cadmium and part of the iron containing materials are solublised. However, lead, silver and gold are not bioleached and remain in the solids. Due to the leaching process, the unleached products are concentrated, and can be separated to form a concentrate which may have considerable commercial value. The lead containing minerals can be mainly converted to insoluble lead sulphate, while the precious metals do not react. Thus, these unreacted materials can be filtered and washed to provide a valuable by-product. Elemental sulphur which is detrimental to smelting, can be contained to less than 0.5% in the residue.

The bioleach solution typically contains zinc, iron (mainly ferric but can also include some unoxidised ferrous), copper, cadmium, plus minor amounts of calcium, magnesium and aluminium. A typical concentration of this solution can be 10 - 50 g/l zinc, 2 - 15 g/l iron, and 0 - 0.5 g/l calcium and aluminium. The amount of copper, cadmium and magnesium can vary depending on the feedstock levels.

The micro-organisms greatly accelerate the leaching of zinc sulphides and generate sufficient ferric ions and

sulphuric acid to stabilise leach conditions. This can eliminate the requirement for external leach reagents.

If the initial feedstock contains copper, and the copper levels in the leached solution are appreciable (ie. about or above 0.5 g/l), the solution containing the zinc (and copper), can be subjected to a process step to remove or extract the copper. This may be achieved by solvent extraction, and a suitable commercial organic extractant can be used (such as LIX984 or ACORGAm5640). The extracted copper can then be recovered as metal in a standard one or two stage solvent extraction/electrowin circuit. This step may be desirable if the feedstock copper levels are high. If the copper levels in the feedstock are moderate (<5% Cu), copper can be recovered in the impurity bleed.

The bioleach solution may be subjected to an iron precipitation step, as ferric iron, and to some extent aluminium, can poison, or be detrimental to, the zinc solvent extraction step. The iron may be precipitated by neutralising the bioleach solution, and typically, the bioleach solution can be neutralised to a pH of about 3 to about 5. The iron precipitation step can be conducted in a well agitated, aerated reactor, and a suitable neutralising agent may include lime, limestone, magnesium oxide or magnesium carbonate. Aeration of the solution may be required to convert any ferrous iron to ferric iron. The iron precipitation step may be conducted at room temperature or elevated temperature and typically a temperature range of 20°C - 90°C can be used. An advantage of the higher temperature, is that the iron precipitates as a readily compact goethite. However, to obtain this, external heating of the solution is needed, and this may be detrimental in energy terms. The residence time required in the iron precipitation step can be dependent on the reaction temperature. For instance, at a pH of 4, a resident time of 2 - 5 hours is usually required to eliminate the ferrous iron at 40°C. At elevated temperatures (ie. 80°C), only 1 - 2 hours may

be required.

If the bioleach solution is neutralised without heating, a more bulky ferric hydroxide precipitate can be formed which is not readily disposable to a tailings dam. The ferric hydroxide precipitate may be further solidified by a high density sludge process, whereby the solid precipitate is recycled in order to act as a nucleating seed. In this manner, a more compact residue can be formed and can have a volume of only 5% - 10% of that of the original ferric hydroxide precipitate.

The iron precipitate is typically the only residue formed in the current process. This precipitate can be utilised in cement manufacture in certain localities, or may meet United States EPA standards for residue disposal. The iron precipitation step may be conducted in a plurality of reactors which may be connected in series, and each reactor may be fitted with aeration facilities. As mentioned above, the carbon dioxide liberated in the iron precipitation step, can be used in the initial bioleach step.

The zinc can be removed from the bioleach solution by a zinc solvent extraction process. The zinc solvent extraction process can separate zinc from remaining impurities (particularly copper, cadmium, calcium and magnesium) and can produce a good quality zinc electrolyte suitable for producing SHG (Special High Grade 99.99% min) cathode zinc at high current efficiencies during a zinc electrowin step.

The solvent extraction step can use commercially available zinc extractants such as D2EHPA and IONQUEST 801. These extractants can be at concentrations of between 10% to 50% extractant and may be in a suitable diluent such as Shellsol 2046.

The solvent extraction step may comprise one or more extract stages whereby zinc can be removed from the aqueous feed solution. The aqueous feed solution can be acidic to prevent or minimise zinc loss, and typically a pH range of about 2 to about 5 is used. After extraction

of zinc into the solvent, the remaining solution (raffinate) can be neutralised. It is preferred that the neutralisation is conducted with a high quality lime or limestone to produce a commercially saleable grade gypsum.

Some un-neutralised raffinate containing between 20 - 30 gpl sulphuric acid can be recycled to the bioleach stage to meet the acid demand of the bioleach stage.

Using the solvent extraction step, it is found that about 10 - 15 g/l of zinc can be removed from the feed solution in each solvent extraction stage when 20% - 30% D2EHPA is used as an organic extractant at an organic:aqueous ratio of 3:1 or higher. Therefore, if the feed solution contains more than 10 - 15 g/l of zinc, a plurality of extraction steps may be required. For instance, a feed solution of 25 g/l zinc may require at least two stages of extraction.

The organic solution, containing extracted zinc may be purified from any entrained aqueous solution and any co-extracted impurities. This may be conducted in one or more scrubbing stages which may utilise either a acidified solution or zinc sulphate solution. A small bleed of electrolyte can be used to acidify the scrub solution, if desired. It is found that at a scrub organic:aqueous ratio of 10-40:1, almost all of the copper, cadmium and most of the calcium can be scrubbed. As some zinc losses can occur during the scrubbing stages, the final scrub liquor can be directed back to either the solvent extraction feed or the bioleach. If desired, a further cleaning stage can be used to remove any entrained scrub solution. This further cleaning stage may comprise an organic centrifuge. This additional stage can ensure a good quality zinc electrolyte.

The purified organic solution can be stripped of zinc by contacting it with spent electrolyte from a zinc electrowinning stage. One or more stages of stripping

may be required to remove substantially all of the zinc from the organic solvent. The zinc electrolyte can be provided with a zinc concentration of 40 - 120 g/l zinc, and preferably 50 - 60 gpl which is suitable for zinc electrowinning.

An advantage of the solvent extraction is that acid which is generated can be neutralised using inexpensive reagents (such as lime or limestone) to produce a commercially valuable product such as gypsum.

The zinc depleted aqueous solution from the solvent extraction step or steps, can be recycled to the bioleach step. The acidity of the recycled solution may be adjusted by adjusting the degree of neutralisation after the solvent extraction step. Thus, if the bioleach is a nett acid consumer, the solvent extraction acid neutralisation can be adjusted to ensure that no additional acid is required for addition at the bioleach stage.

If desired, a portion of the final solution can be recycled through the zinc solvent extraction step or steps to dilute the feed liquor so as to ensure that the zinc concentration in the feed is controlled. For instance, by diluting the zinc concentration to about 15 - 20 g/l, only a single acid neutralisation stage may be required.

If the solution is recycled to the bioleach step, it may be necessary to periodically remove some of the impurities to prevent buildup in the process liquor. These impurities may comprise cadmium, magnesium and copper. Therefore, a bleed stream may be provided which will remove the impurities. The bleed stream may be treated by a zinc dust treatment to remove cadmium and copper from the bleed liquor. This can produce a copper/cadmium cement which may be commercially valuable.

The resultant solution may be neutralised to precipitate zinc and other dissolved metals from the solution. This may be achieved by adding lime or limestone to the solution. The precipitate may then be

recycled to the solvent extraction stage to recover the zinc. The final neutralised solution may contain magnesium and halogens such as chlorides and fluorides but may substantially be free from heavy metals and can be disposed of as an effluent in a safe manner.

As a variation, ammonia can be utilised as an acid neutralisation agent in the solvent extraction stage. This can eliminate the need for multiple stages of extraction coupled with acid neutralisation. A single extraction stage with two to four extract units in series can be used, and an organic:aqueous ratio of 3-5:1 could be employed. The ammonia can be recovered by lime neutralisation according to known techniques.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram of the process according to an embodiment of the invention.

Figure 2 is a flow diagram of the process showing a two stage extraction of zinc from solvent.

Figure 3 is a flow diagram of the process showing a single stage extraction of zinc from solvent.

BEST MODE

Bioleach Stage

Referring to figure 1, a mixed lead/zinc sulphide concentrate 10 assaying at 37% zinc, 6% iron, 0.7% copper and 14% lead was slurried in water to produce a 6.5% w/w slurry. Additional ammonia (as commercial grade ammonium sulphate fertiliser) and phosphate (as commercial grade fertiliser) were added to provide sufficient nitrogen and phosphorus for bacterial growth.

The slurry was fed to a fully continuous bioleach train 11, with the temperature controlled at 40°C and the pH at 1.6 - 1.8. The aeration was maintained at 0.4 vvm with the addition of 2% carbon dioxide as a carbon supplement. In total, the working volume of the bioleach train was 8L (2x4L reactors).

The slurry was inoculated in an adapted mixed bacterial population of T. Ferrooxidans, L. Ferrooxidans, Thiobacillus Thiooxidans, Sulfobacillus strains and mixed

heterotrophic organisms prior to commencing continuous operation. Following this, the chemical and biological response of the system was monitored for several overall residence times. Sufficient time was allowed at each residence time to ensure that steady state behaviour was obtained.

Table 1 presents the bioleach results found over an overall residence time range of 1.4 - 5 days. The overall zinc extraction was in the range 91% - 97%, depending on residence time. Specific zinc extraction data shows that 80% - 90% of the zinc extraction occurred in the first vessel. The copper and iron extractions varied with residence time, but were typically 55%-70% and 45% - 65% respectively. The acid demand was a low 45 - 50 kgs of H_2SO_4/tonne of feed solids at residence times over 2 days, rising to 80 - 90 kgs/tonne at 1.5 days overall residence time.

The results show that bioleaching of the mixed lead/zinc concentrate was an efficient and effective technique for solubilising the zinc. All of the lead, gold and silver in the head material reported to the Pb/Ag/Au concentrate, resulting in a saleable byproduct with 35% - 40% Lead. No elemental sulphur was detected.

TABLE 1 BIOLEACH EXTRACTION RESULTS USING A MIXED LEAD/ZINC CONCENTRATE FEEDSTOCK

(35% - 40% Zn, 14% Pb, 0.7% Cu, 6% Fe)

Overall Residence Time (days)	Feed Solids Content (%)	Metal Extraction (%)		Specific Zinc Extraction (g/l - day)	
		Zinc	Copper	Vessel 1	Vessel 2
4	6-8	97	76	16.2	0.8
3	6-8	96.5	74	22.5	3.2
2.2	6-8	94.5	67	24.4	3.8
1.5	6-8	94	67	27.6	3.3

If necessary, the bioleach solution is subjected to a copper solvent extraction, electrowinning step 12. This is only required if the copper concentration in the bioleach solution is above 0.5 g/l.

Iron Precipitation Stage

Subsequent to any optional copper solvent extraction/electrowinning step, the bioleach solution is subjected to an iron removal step 13. In the iron removal step the bioleach solution containing 31gpl zinc and 6gpl iron is placed in a 1 litre reactor with copius aeration. The temperature is maintained at 40°C and the pH is adjusted to about 4.0 using powdered limestone additions. After about 3 to 4 hours, the agitated and aerated slurry was allowed to settle in a 1 litre settling vessel. The solution iron level was reduced to less than 5 ppm with less than 2% zinc loss. The final washed dry precipitate was assayed at 13% iron and 2% zinc. A difficulty was poor settling characteristics, with a settling rate of only 0.14mm/min. The solids density was only 18% w/w.

In order to improve precipitation behaviour and particularly the settling characteristics, the ferric hydroxide/gypsum precipitate is recycled to act as fresh seed for further precipitation. This procedure was conducted at a temperature of 40°C and was repeated 9 times. The result was that the zinc loss to the precipitate was reduced from 2% zinc to 0.3% - 0.4% zinc. The solids were much more readily filterable, and the settling rate increased from 0.14 mm/min to 2.4 mm/min, even with 9 times the mass of precipitate. The ultimate solids density, again with 9 times the mass of material, reduced to 39%. Thus, the volume of the final precipitate in a bioleach process could be reduced to 5% - 10% of that of only a single pass precipitation.

As mentioned above, the iron precipitation step 13 could be subjected to a heating step, as at elevated temperatures, the iron precipitates as a more readily compact goethite. The copious aeration in the iron precipitation step is necessary to ensure that all ferrous iron is oxidised to ferric. The carbon dioxide liberated by the neutralisation agent can be recycled as shown in 14 back to bioleach step 11. A number of iron

precipitation steps may be required.

Solvent Extraction of Zinc

After the iron precipitation step 13, the bioleach solution is subjected to a continuous zinc solvent extraction train 15. Prior to solvent extraction, the bioleach solution assays at 30 g/l zinc, 190 ppm calcium, 440 ppm magnesium and 110 ppm cadmium. The zinc solvent extraction train 15 comprises a plurality of separate zinc solvent extraction steps 16, 17, 18 the number of which will depend primarily upon the concentration of zinc in the bioleach solution (zinc tenor). In the first step 16, the bioleach solution is subjected to extraction with an organic solvent comprising 25% D2EHPA in Shellsol 2046. In the first step 16, the zinc tenor was reduced from 30 g/l zinc in the feed to 14 g/l in the raffinate (the remaining bioleach solution). The organic solvent is separated and passed to a scrub stage 19 where it is scrubbed with 5 g/l zinc in 7.5 g/l sulphuric acid (ie. diluted zinc electrolyte obtained from the zinc electrowin step 20). Subsequent to the scrub stage 19, the solvent is stripped at a strip stage 21, the stripping liquid being the zinc electrolyte from the zinc electrowin step 20. The stripped solvent is recycled back through the zinc solvent extraction train 15. If the zinc tenor is high, further zinc solvent extraction steps 17, 18 may be necessary. The bioleach solution is adjusted to a pH of about 4 before passing into zinc solvent extraction step 16, and subsequent to being extracted, is neutralised with high quality lime or limestone to produce a commercially valuable gypsum 22. The neutralisation step is carried out after each zinc solvent extraction step 16, 17, 18 as shown in the figure. The resultant neutralised bioleach solution (ie. raffinate) is recycled through 23 back to the bioleach step 11. A portion of the raffinate is bled through line 24 to zinc solvent extraction step 16 to dilute the zinc tenor to an acceptable level thereby minimising the number of solvent extraction steps required. As the

recycling of the raffinate will result in increased impurity levels, a bleed stream 25 is provided. The bleed stream 25 is treated initially by zinc dust to remove cadmium and copper and to produce a cadmium/copper cement. The resultant solution is then neutralised with lime or limestone to precipitate zinc and other dissolved metals from solution, and these precipitated compounds are then recycled to the zinc solvent extraction step 16. The remaining neutralised solution is an effluent liquor which can contain magnesium but will not contain heavy metals such as cadmium, copper or zinc.

Figure 2 shows a specific two stage extraction process.

Two Stage Extraction

The neutralised liquor 30 from Iron Neutralisation and Residue Filtration, assaying at 30 gpl Zinc, 190 ppm Calcium, 440 ppm Magnesium and 110 ppm Cadmium was directed to a fully continuous Zinc Solvent Extraction apparatus with 500 cc mixers and 2L settlers. The solvent extraction train, as depicted in Figure 2, had the following operating characteristics:

Organic: 25% D2EHPA in Shellsol 2046

Strip Liquor: 60-70 gpl Zinc, 180-200 gpl Sulphuric Acid

Scrub Liquor: 5 gpl Zn, 7.5 gpl H_2SO_4 (Diluted Zinc Electrolyte).

Extract Circuit: 2 stages of Extraction 31, 32, each comprising 2 Contacting Units; 31A,B 32A,B; Organic/Aqueous Ratio = 3:1, 2 minutes Residence Time; Organic Continuous.

Scrub Unit: 1 stage of Scrubbing, comprising 2 Contacting Units 33, 34; Organic/Aqueous Ratio = 20:1; 2 minutes Residence Time; Aqueous Continuous.

Strip Unit: 1 stage of Stripping comprising 2 Contacting Units: 35,36; Organic/Aqueous Ratio = 4:1; 2 minutes Residence Time; Organic Continuous.

The trial was conducted over a 24 hour period to determine the steady state metallurgical response of the system.

The results indicate that the zinc tenor was sequentially reduced from 30 gpl in the feed to 14 gpl (Stage 1 Extraction) and 5 gpl (Stage 2 Extraction). Only calcium was noticeably transferred to the organic in the extract stages (the raffinate was 100 ppm compared to 190 ppm in the feed). Scrubbing removed 62% of this transferred calcium, resulting in a final electrolyte containing 10 ppm Ca. Copper, cadmium, aluminium and magnesium levels in the electrolyte were below detection levels. The zinc loss in scrubbing was less than 1%, but this would be recovered by directing the scrub raffinate back to the bioleach or solvent extraction feed.

Single Stage Extraction

In a modification of the two stage extraction process, a proportion of neutralised zinc raffinate 40 can be recycled to the solvent extraction feed 30, thus reducing the initial zinc tenor. The benefit of such a modification is a reduction in the number of extraction stages required, but, at the expense of increased throughput. Figure 3 illustrates the required changes in system configuration.

Two 24 hour fully continuous trials were conducted using recycle ratios of both 1:1 (Recycle Flowrate: Feed Flowrate) and 2:1 respectively, using the configuration of Figure 3. Other conditions were as per the two stage extraction example. In lieu of 4 Extract Contacting Units, only 2 were employed, using the recycle strategy.

At a recycle ratio of 1:1, with a feed of zinc tenor 32 gpl, a final raffinate of 2.5 gpl Zn was obtained. Again, no significant levels of copper, cadmium, aluminium, and magnesium were transferred to the loaded zinc electrolyte. About 50 ppm Ca was transferred.

Using a higher recyle ratio of 2:1, the final raffinate zinc tenor reduced to less than 1 gpl. Again, apart from calcium, no significant impurity transfer to

the loaded electrolyte was noted. The calcium scrubbing efficiency, with 2 Scrubbing Contactors was about 50%.

In summary, zinc solvent extraction of bioleach solutions, using either single or multiple extraction stages provides an economic and attractive method for recovering the zinc in bioleach solutions into a zinc electrolyte suitable for zinc electrowinning.

Electrowinning of Zinc

Loaded electrolyte solutions containing 50 - 100 g/L Zn^{2+} and 140 - 180 g/L H_2SO_4 were prepared from zinc electrolyte generated from the continuous solvent extraction trials. Cu, Ni, Co, Cd, Ag, Pb, Fe, Sn, Cr and Sb electrolyte impurity levels were found to be within the limits required for SHG grade zinc electrowinning. Dissolved and entrained organic components were removed from the electrolytic solutions by passing them through an activated carbon column prior to electrowinning.

Parallel plate electrowin trials were performed to determine the effects smoothing agent additions (glue, guartec, antimony tartrate etc), current density, anode preparation, Zn^{2+} and H_2SO_4 tenor have on Zn plate morphology and the current efficiency of the cell. The following range of conditions were employed in laboratory electrowin trials:

- Polished Al cathodes and Pb (0.5% Ag) anodes previously passivated through electrolysis in KF/Na_2SO_4 electrolyte
- Electrodes with a centre to centre spacing of 50 mm
- Electrolyte residence time of 120 minutes
- Electrolyte solution of 35 - 40°C
- Continuous electrolyte and smoothing agent addition (10-60ppm)
- Current densities of 350 - 500 mA/M^2
- Cell voltage 2.5 - 3.5 V

The results of the electrowin trials indicated that the morphology of the Zn deposit was found to be heavily dependent on the electrolysis conditions. In laboratory

trials smooth and compact Zn deposits were produced with high current efficiencies (over 90%) when the electrowin cell was run at current densities of 350 - 450 A/m^2 at ~35°C. Power consumption data for these trials was in the order of 2575 - 3000 kWhr/t of Zn.

In summary Zn electrowin provides an efficient method for recovering Zn from electrolyte solutions produced from Zinc solvent extraction unit operations. An electrowin cell operating at 425 A/m^2, 36°C, 2 hour residence time and 40 ppm guartec yielded current efficiencies of approximately 92% with a laboratory scale power consumption of around 2900 kWhr/t of Zn.

Bench Scale Example of the Bioleaching at a Commercial Zinc Concentrate using Tailings Solids Recycle.

A mixed lead/zinc sulphide concentrate assaying at 48% Zinc, 10% Iron, and 2.7% Lead was slurried in water to produce a 6% w/w slurry. Additional ammonia (as commercial grade ammonium sulphate fertiliser) and phosphate (as commercial grade fertiliser) were also added to provide sufficient nitrogen and phosphorous for bacterial growth.

The slurry was fed to a fully continuous bioleach train, with the temperature controlled at 40°C and the pH at 1.6 - 1.8. The aeration was maintained at 0.4 vvm with the addition of 2% CO_2 as a carbon supplement. In total, the working volume of the bioleach train was 8L, comprising three reactors in series of volume 4L, 2L and 2L respectively.

In order to improve zinc recoveries, the final tailings slurry (from Vessel 3) was directed to a Tailings Thickener which produced a relatively clear overflow, and a concentrated underflow slurry containing the tailings solids. On a daily basis, a predetermined amount of tailings slurry (typically 80-90%) was recycled to the first Bioleach reactor. In such a fashion unreacted zinc sulphide was recycled to improve the extraction.

The slurry was inoculated in an adapted mixed

bacterial population of T. Ferrooxidans, L. Ferrooxidans, Thiobacillus Thiooxidans, Sulfobacillus strains and mixed heterotrophic organisms prior to commencing continuous operation. Following this, the chemical and biological response of the system was monitored for several overall residence times. Sufficient time was allowed at each residence time to ensure that steady state behaviour was obtained.

Table 2 Bioleach Extraction Results using a Commerical Zinc Concentrate with Tailings Solid Recycle (45-50% Zn, 10-11% Fe, 2-3% Pb)

Overall Residence Time	Feed Solids Content	Tailings* Recycle	Metal Extraction		Specific Zinc Extraction (g/L - day)		
(days)	(%)	(%)	Zinc	Iron	Vessel 1	Vessel 2	Vessel 3
3.7	6 - 7	90	94	76	12.1	2.9	0
3	6 - 7	90	94	70	13.9	5.1	0
2.5	6 - 7	75 - 80	92	68	12.4	8.0	0.3

* as a proportion of Thickened Tailings Underflow

Table 2 presents the bioleach results found over an overall residence time range of 2.5 to 4 days, with tailings solids recycle in the range 75 to 90%. The overall zinc extraction was in the range 92 to 94%, depending on the overall residence time. Specific zinc extraction data indicates that 60 - 80% of the zinc extraction occurred in the first vessel, with very little extraction occurring in the final bioreactor. The iron extraction varied with residence time, but was typically 70%. The acid demand was a low 30 - 40 kgs of H_2SO_4/tonne of feed solids at residence times over 3 days, rising to 100 kgs/tonne at 2.5 days overall residence time. Product solution tenors were in the range 23 to 27 grams of zinc/kg of solution and 3 to 3.3 grams of Iron/kg of solution.

This example provides a further illustration of the

effectiveness of bioleaching for solubilising zinc from zinc concentrates. The final solution produced from the bioleach is an ideal feedstock for an Iron Neutralisation/Zinc Solvent Extraction/Electrowinning Circuit for producing SHG grade zinc metal.

Fully Continuous Pilot Plant Scale Example for a High-Grade Lead/Zinc Concentrate Feed.

Bioleach Stage

A high grade zinc/lead sulfide concentrate (HGC) assayed an average of 48% zinc, 10% iron, 3% lead and 0.15% copper was slurried in recycled raffinate from a solvent extraction circuit (see below) to give a 6% (w/w) slurry. Additional nitrogen (added as commercial grade ammonium sulfate fertiliser) and phosphate (as commercial grade fertiliser) were also added to provide nitrogen and phosphate at levels where were sufficient to maintain non-limited bacterial growth.

The slurry was fed to a fully-continuous bioleach train, with the temperature of all reactors controlled at 40°C and the pH at 1.6 - 1.7. Recycled scrub solution and un-neutralised raffinate from the solvent extraction circuit were used as a source of acid to maintain the pH in reactor 1 and 2. The aeration was maintained at 0.2 vvm with the addition of 2% CO_2 as a source of carbon for autotrophic bacteria. The slurry was fed at an equal rate into two reactors (reactors 1 and 2) set in parallel. The overflow from both reactors fed into a single series of two reactors (reactors 3 and 4). Each reactor had a volume of 330L, giving a total working volume of 1320 L for the bioleach train. The slurry from reactor 4 was fed to a continuous thickener which produced a relatively solids-free overflow and a thickened underflow. About 90% of the thickened solids were filtered and recycled to reactors 1 and 2, while the remaining 10% was filtered and discarded as a solids bleed. The liquor overflow from the thickener was directed to a continuous iron neutralisation stage.

The bioleach train was inoculated with a mixed

culture of acidiphilic bacteria adapted to growth on the HGC. The inoculum was known to contain species from the genera *Thiobacillus*, *Leptospirillum*, *Acidiphillium* and *Sulfobacillus*. Following inoculation, the chemical and biological response of the system was monitored for 3 months at an overall residence time in the range of 4 to 6 days. Steady state behaviour was established within 1-2 residence times.

Analysis of the chemical assay results obtained indicated that 80 - 90% of the zinc was extracted in reactors 1 and 2. The overall zinc extraction was over 95%, with only a minor loss of zinc in the 10% solids bleed. Typically, the zinc in the bled solids averaged 10% (w/w). Similarly, the percentage of iron extracted was over 80%. The amount of lead in the bled solids ranged between 15 - 20% (w/w). With 90% recycle, there was no solids build-up in the thickener and the solids density remained relatively constant in each of the bioreactors.

The results obtained indicate that bioleaching of a high-grade zinc/lead concentrate with a 90% tailings solids recycle provided an efficient method for solubilising zinc and forming a saleable lead concentrate by-product. No elemental sulfur was detected in the bioleached solids product.

Iron Precipitation Stage

The liquor overflow from the tailings thickener contained on average 18 - 26 gpl zinc and 3-3.5 gpl iron. For iron precipitation, the liquor was fed continuously into a well aerated two reactor series maintained at 40°C and with an overall residence time exceeding 3 hours. The pH in the second reactor was maintained at pH 4 by the continuous controlled addition of limestone as a 30% (w/w) slurry in water.

The final neutralised slurry was filtered through a plate and frame filter press with a total filtration area of 2.8 m^2. Typically, flow rates through the filter averaged 20 - 40 L/min. The filtered solution contained

22 -28 gpl zinc and <5 ppm iron. The final washed dry precipitate assayed an average of 11 - 13% iron and less than 2% zinc. The filtered liquor was of consistent clear quality suitable for direct extraction in the solvent extraction circuit.

Solvent Extraction of Zinc

The neutralised, filtered liquor from the iron neutralisation train assayed at 20 - 30 gpl zinc and <5ppm iron. Other elements assayed in this liquor included copper (25 ppm), cadmium (90 ppm), magnesium (120 ppm) and calcium (600 ppm). The liquor was fed to a fully continuous solvent extraction circuit consisting of 4 extraction, 2 stripping and 2 scrubbing units, each with a mixer volume of 16L and a settler volume of 116L. The operating characteristics for the solvent extraction circuit were identical to those presented previously.

The inclusion of an interstage neutralisation between extraction passes allowed the zinc tenor to be sequentially reduced from 25 - 30 gpl in the feed to 15 gpl (stage 1 extraction) to 4 gpl (stage 2 neutralisation) in the final raffinate. The raffinate from each extraction stage was neutralised with a 30% w/v limestone slurry to pH4 and filtered using a plate and frame filters. The final neutralised raffinate was recycled to the bioleach train to prepare further feed, except for a small bleed (typically less than 5%) which allowed removal of copper, cadmium, magnesium and halogens.

The zinc was stripped from the loaded organic phase using a strip solution containing 150-180 gpl sulfuric acid and 55 - 65 gpl zinc, producing a loaded zinc electrolyte containing 90 gpl zinc and less than 20 ppm iron. This electrolyte was of suitable quality for electrowinning after passage through an activated carbon column to remove any entrained or dissolved organic from the solvent extraction circuit.

It can be seen from the above results that the use of bioleaching to solubilise zinc from a high grade

concentrate with solvent extraction and electrowinning to recover the zinc was scaled up successfully from a bench-scale operation to a fully continuous Pilot Plant. The Pilot Plant operation was robust, with few processing problems experienced.

It can be seen that the integrated bioleach/solvent extraction system provides a low capital and operating cost route for treating materials which are difficult to handle in conventional processes. The bacteria in the bioleach step generates the leach reagents required to solubilise the zinc and therefore eliminates the need for purchasing or producing reagents on site. Low capital costs are achieved because of the simplicity of the unit operation stages, the ability to conduct the entire process at atmospheric pressures (thereby eliminating the need for pressurised vessels), and the ability to conduct the entire process at room or slightly elevated temperatures (thereby saving on energy costs). Most equipment can consist of tanks only and only low cost reagents such as limestone need to be constantly added.

The process is particularly suited to treating low grade zinc concentrates or mixed lead/zinc concentrates. Both of these materials have limited value given current and projected metal prices.

The process is highly flexible and ideal for stable automatic control. A high equipment availability (over 95%) would be expected from a commercial operation.

Because of the simplicity of the process, manpower usage can be minimised. Maintenance costs would also be accordingly reduced.

In terms of feedstock, the bioleach process is quite robust. Particular problems to alternative processes, such as high magnesium levels and elemental sulphur contents will not hinder the current invention. To some degree, halogens can be tolerated, in contrast to electrolytic plants.

The process has been designed to incorporate significant environmental advantages. No gaseous

effluents exist. Aside from the iron residue, all byproducts can be commercially sold. Considerable effort has been devoted to minimise the volume of the iron residue and to ensure it meets EPA regulations. In certain localities, this residue could be sold.

Various other changes and modifications can be made without departing from the spirit and scope of the invention as claimed.

CLAIMS:

1. A method for separating zinc from zinc concentrates comprising the steps of subjecting the zinc concentrate to a bioleach step to form a bioleach solution containing zinc, at least partially removing the zinc from the solution and recycling at least part of the zinc depleted solution to the bioleach step.

2. The method of claim 1, wherein the pH of the recycled zinc depleted solution is adjusted to ensure that no additional acid is required for addition at the bioleach step.

3. The method of claim 2, wherein the pH of the zinc depleted solution is adjusted with lime or limestone to produce a commercial grade gypsum.

4. The method of claim 1, wherein the bioleach step does not dissolve lead, silver and gold in the zinc concentrate, thereby producing a solid concentrate of lead, silver and gold which is separated.

5. The method of claim 1, wherein iron in the bioleach solution is removed prior to at least partially removing the zinc from the solution.

6. The method of claim 5, wherein iron is precipitated from the bioleach solution by adjusting the pH of the bioleach solution to between 3 - 5.

7. The method of claim 6, wherein the iron is precipitated at a temperature less than that required to produce goethite, and the precipitate is recycled a plurality of times to act as nucleating seed for further precipitation thereby improving the settling rate and separability of the precipitate from solution.

8. The method of claim 7, wherein the pH is adjusted using a carbonate and CO_2 liberated by the neutralisation step is at least partially recycled to the bioleach step to provide a source of carbon.

9. The method of claim 5, wherein the bioleach solution is contacted with a zinc extracting organic solvent to at least partially remove zinc from the bioleach solution.

10. The method of claim 9, wherein acid in the zinc

depleted solution is neutralised with lime or limestone to produce a commercial grade gypsum.

11. The method of claim 9, wherein at least part of the zinc depleted solution is recycled to the bioleach step and the pH of the solution is adjusted to meet the acid demand of the bioleach step.

12. The method of claim 11, wherein a portion of the recycled solution is fed back to the zinc extracting step to dilute the incoming bioleach solution to provide a zinc concentration advantageous for extraction.

13. The method of claim 11, wherein a portion of the recycled solution is treated to prevent excessive build-up of metals such as cadmium, magnesium and copper.

14. The method of claim 13, wherein cadmium and copper are removed by a zinc dust treatment, the resultant solution is neutralised to precipitate zinc and other dissolved metals, the zinc is recycled to the solvent extraction stage and the remaining solution containing magnesium is removed.

15. The method of claim 9, wherein the organic solvent containing zinc is purified from entrained bioleach solution co-extracted impurities.

16. The method of claim 15, wherein the organic solvent is scrubbed by contact with an acidified aqueous solution to remove copper, cadmium and calcium, and the scrub liquor is directed to the solvent extraction step to remove any zinc.

17. The method of claim 15, wherein the purified organic solvent is stripped of zinc by an electrowinning stage.

18. The method of claim 1, wherein bioleaching is carried out using micro-organisms selected from the group consisting of the aerobic autotrophs Thiobacillus Ferrooxidans and Leptospirillum Ferrooxidans, and preferably T. Ferrooxidans, L. Ferrooxidans, Thiobacillus Thiooxidans, Sulfobacillus strains and mixed heterotrophic organisms.

19. The method of claim 18, wherein the bioleach step is carried out at a pH of between 0.5 - 2.5, a temperature

range of between 20 - 80°C, a time of between 0.5 - 10 days and under aerobic conditions.

20. The method of claim 19, wherein a plurality of aerated reactors are provided in series.

21. The method of claim 9, wherein a plurality of solvent extraction stages are provided with the pH of the aqueous solution being adjusted to pH 2 - 5 prior to each solvent extraction stage.

22. The method of claim 9, wherein a copper solvent extraction/electrowinning stage is provided prior to iron removal or in the treatment stage of claim 13, if the copper level in the bioleach solution is greater than 0.5 gpl.

Fig.1.

SCHEMATIC OF THE ZINC SULPHIDE BIOLEACH PROCESS.

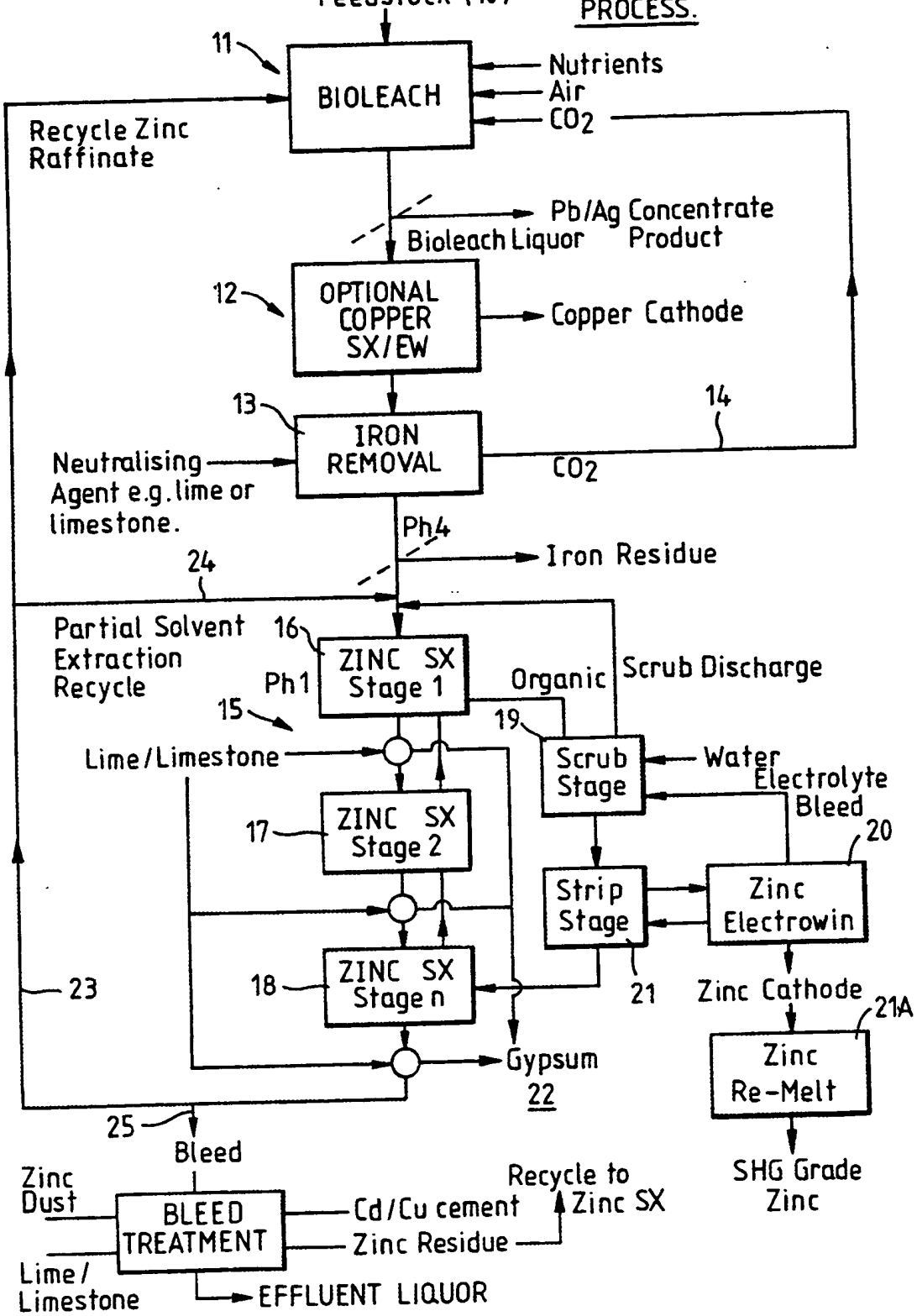


Fig. 2. FLOWSHEET OF CIRCUIT WITH TWO STAGE EXTRACTION

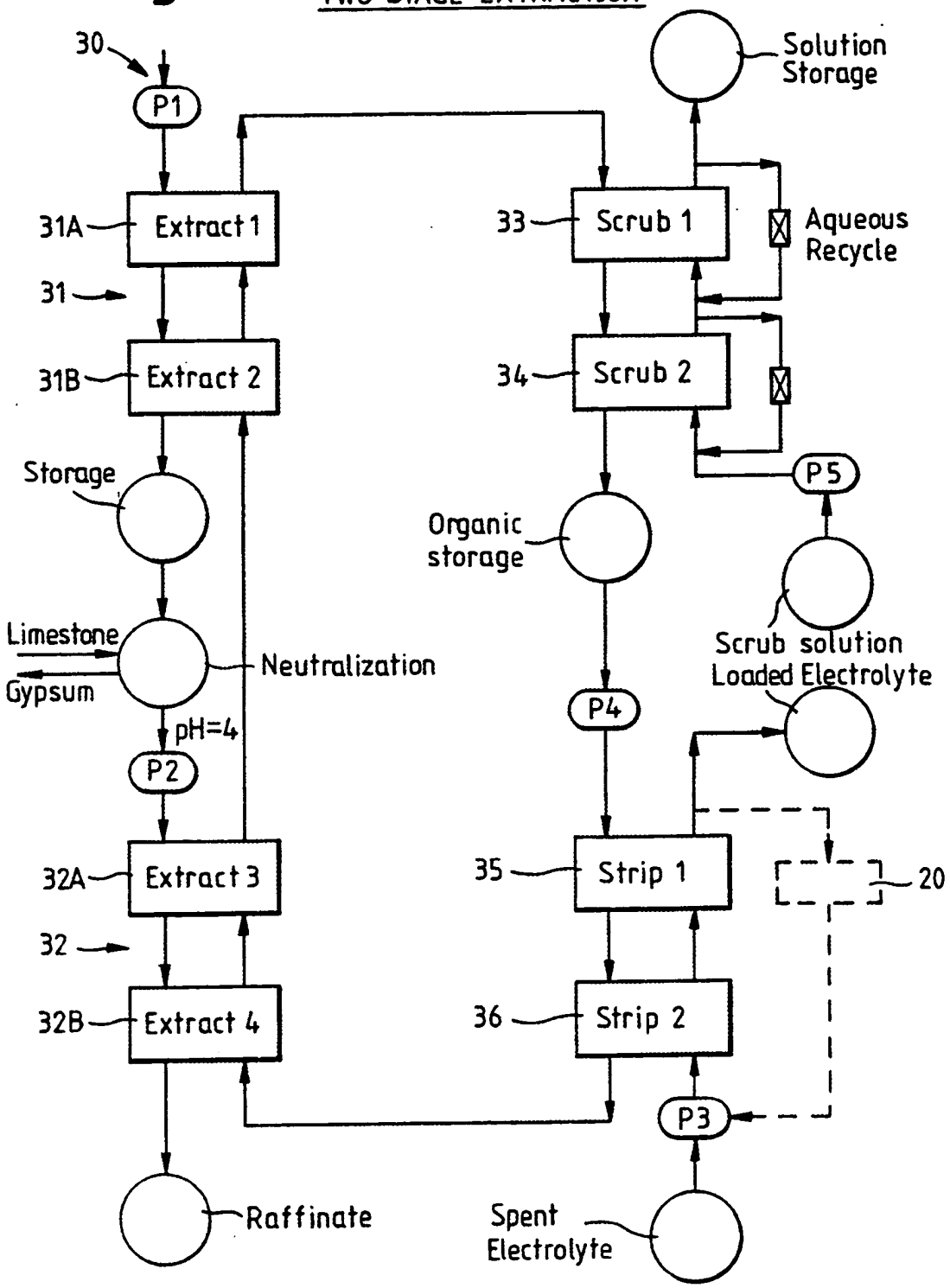
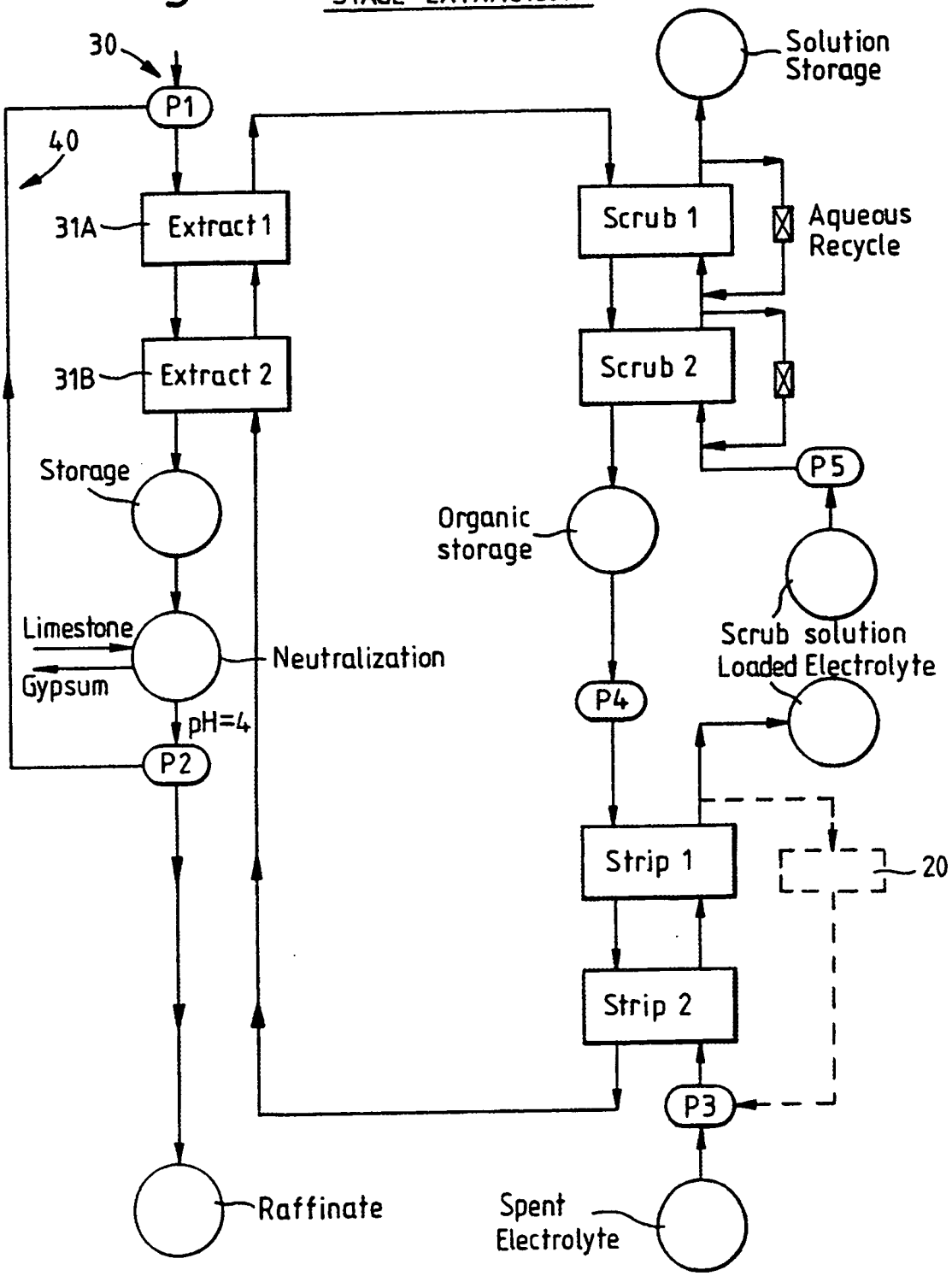


Fig.3. FLOWSHEET OF CIRCUIT WITH SINGLE STAGE EXTRACTION



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 94/00266

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.[6] C22B 3/18 // C22B 19:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC C22B 3/00, 3/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT : (Zinc or Zn and Bioleach: or Microorg:)
JAPIO : (Zinc or Zn and Bioleach: or Microorg:)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
P,X	US,A, 5278069 (FASS, R.L. et al.) 11 January 1994 (11.01.94) see col 1 lines 29-40, col 2 line 46 - col 3 line 25, col 3 lines 36-51, Fig 3	1-13,15-22
X	AU,B, 56748/65 (292916) (BRITISH COLUMBIA RESEARCH COUNCIL) 29 September 1966 (29.09.66) see page 8 lines 30-32, Fig 4, page 1 - page 2	1-22
A	Journal of Metals, Metallurgical Society of AIME, Volume 41, No 6, 1989, Torma, A.E.., "The Microbiological Extraction of Less Common Metals", pages 32-35 whole document	1

[X] Further documents are listed in the continuation of Box C.

[] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 September 1994 (01.09.94)	8 Sept 1994 (08.09.94)
Name and mailing address of the ISA/AU	Authorized officer
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	US,A, 2829964 (ZIMMERLEY, S R et al.) 8 April 1958 (08.04.58) whole document	1
A	Derwent Abstract Accession No 89-366136/50, Class D16, J01, M25, ES,A, 2009104 (RIO TINTO MINERA SA) 16 August 1989 (16.08.89) Abstract	1-22
A	Derwent Abstract Accession No 83-849319/51, Class M25, SU,A, 998549 (URALS UNIPROMED) 23 February 1983 (23.02.83) Abstract	1-22
A	Derwent Abstract Accession No 06496K/03, Class D16, M25, SU,A, 910815 (MOSCOW STEEL ALLOYS INST) 7 March 1982 (07.03.82) Abstract	1-22
A	AU,A, 11201/92 (MOUNT ISA MINES LIMITED) 3 September 1992 (03.09.92) whole document	1-12

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member
US	5278069	NIL
AU	56748/65	NIL
US	2829964	NIL
ES	2009104	NIL
SU	998549	NIL
SU	910815	NIL
AU	11201/92	NIL
		END OF ANNEX